



Building global change resilience: Concrete has the potential to ameliorate the negative effects of climate-driven ocean change on a newly-settled calcifying invertebrate

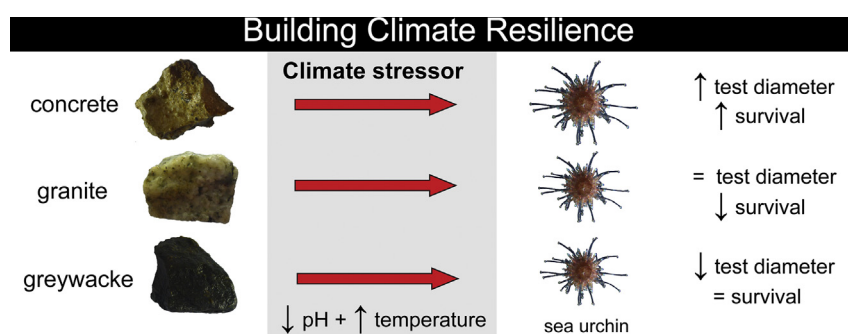
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HIGHLIGHTS

- Coastal protection structures need to be upgraded in response to rising sea levels.
- Upgrades using pH-buffering concrete may shield colonizers from ocean acidification.
- We settled sea urchins on concrete and rocks in ocean conditions predicted by 2100.
- Concrete inhibited settlement, but had positive effects on growth and survival.
- Concrete shows potential for responding to sea level rise and ocean climate change.

GRAPHICAL ABSTRACT



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ABSTRACT

Global climate change is driving sea level rise and increasingly frequent storm events, which are negatively impacting rapidly-growing coastal communities. To mitigate these impacts, coastal infrastructure must be further protected by upgrading hard defences. We propose that incorporating pH-buffering materials into these upgrades could safeguard marine organisms from the adverse effects of ocean acidification and ocean warming during the vulnerable transition from planktonic larvae to benthic juveniles. To test this, we examined the effects of ocean warming (24 or 27 °C), ocean acidification (pH 8.1, 7.9, 7.7), and substratum (concrete, greywacke, granite) in all combinations on the settlement success of an ecologically and commercially important sea urchin, *Tripneustes gratilla*. Low pH (7.9, 7.7) generally reduced the quantity and size of juveniles four weeks post-settlement, although this was partially ameliorated by increased temperature (24 vs. 27 °C). In the warmed and acidified treatments, settlement rates were lower on concrete than granite or greywacke, but two weeks post-settlement, juveniles on concrete were larger, and had longer spines and higher survival rates than on greywacke or granite, respectively. The benefits provided by concrete to newly-settled juveniles may be related to alkali chemicals leaching from concrete buffering low pH conditions in surrounding seawater and/or increased availability of bicarbonate in the boundary layers around its surface. Our results highlight the potential for pH-buffering materials to assist marine organisms in coping with the effects of changing ocean conditions, but further research is required to understand the generality and mechanism(s) driving the beneficial effects of concrete and to test pH-buffering materials in the field.

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1. Introduction

Increases in atmospheric CO₂ levels are changing the world's oceans. By 2100, average open ocean conditions are predicted to be 0.5–4 °C warmer and 0.1–0.4 pH units lower than conditions at present (IPCC, 2014). Global climate change is also accelerating sea level rise and changing the frequency and/or intensity of storms (Knutson et al., 2010; Nicholls and Cazenave, 2010), with projected detrimental socio-economic impacts on human populations through erosion, submergence, flooding, and saltwater intrusion into groundwater (Turner et al., 1996; Nicholls and Cazenave, 2010). To limit the potential impacts of climate-driven ocean change on human settlement, agriculture, trade, industry, and amenity, the protection of coastal infrastructure will be increasingly important (Nicholls and Cazenave, 2010).

Construction of hard defences, such as breakwaters, groynes, seawalls, and dykes, is a conventional strategy to manage the adverse effects of changing ocean conditions. Hard defences are common along the world's coastlines, comprising up to 70% of the coast in some regions (Dugan et al., 2011), and are major components of the nearly 4000 linear km of artificial waterways in estuaries globally (Waltham and Connolly, 2011). Existing hard defences will need to be upgraded or replaced in coming decades to counter sea level rise (Hanson et al., 2011; Hallegatte et al., 2013; Arns et al., 2017), as it is unlikely that the economically and socially valuable areas protected by these structures will be abandoned (Waltham and Connolly, 2011; Jamero et al., 2017). The necessity to upgrade existing infrastructure and construct new hard defences provides an opportunity to engineer these artificial structures to provide additional benefits beyond their primary role of coastal defence, such as improved habitat for marine organisms (Davis et al., 2017).

Hard defences provide habitat for a range of estuarine and marine organisms (reviewed by Bulleri and Chapman, 2010) that support ecosystem services, such as nutrient cycling, improvement of water quality, and production of seafood (Wilkinson et al., 1996; Airolidi et al., 2005). The types of ecological communities that develop on artificial structures are influenced by species availability, age of structure, habitat complexity, orientation of substrata, and type of substratum (e.g. Glasby, 2000; Whorff et al., 2009; Burt et al., 2011). A greater understanding of the role of these factors in determining community structures has enabled engineering solutions that boost the abundance and/or diversity of organisms on hard defences (Strain et al., 2018), with the potential to provide additional benefits such as increased longevity of artificial structures through enhanced corrosion-resistance (Kawabata et al., 2012). Progress on improving the habitat provided by hard defences will require knowledge about interactions among marine organisms, building materials, and changing ocean conditions, which is currently lacking (Parsons et al., 2014).

Concrete and natural rock materials (e.g. granite, greywacke, sandstone) are typical components in hard defences (Bulleri and Chapman, 2010) and are materials likely to be used to protect coastal infrastructure in response to climate-driven ocean change. The physical and chemical properties of these materials affect the way in which they interact with surrounding seawater over time periods of at least one decade (e.g. Jefferies, 1987; De Weerd et al., 2014), with implications for the diversity and abundance of the biota that colonise these substrata (Fitzhardinge and Bailey-Brock, 1989; Anderson, 1996; Glasby, 2000). For example, the surface of concrete reacts with seawater to form Mg (OH)₂ and CaCO₃ precipitates (Buenfeld and Newman, 1986). Concrete may also leach Ca(OH)₂ (Anderson and Underwood, 1994). Alkali chemicals leaching from concrete increase the pH of the concrete's surface and can influence the carbonate chemistry of surrounding water (Anderson and Underwood, 1994; Davies et al., 2010; Wright et al., 2011), an effect that may be amplified as oceans warm and become more acidic as predicted for the near future.

Ocean acidification and ocean warming are predicted to have profound negative effects on calcifying organisms (Kroeker et al., 2010;

Kroeker et al., 2013), including sea urchins which experience reduced growth, survival, and reproductive success when grown in ocean conditions predicted to occur by 2100 (reviewed by Wittmann and Pörtner, 2013; Przeslawski et al., 2015). The effects of ocean change on sea urchins are concerning given the importance of these herbivores in shaping community structure (Kitching and Ebling, 1961; Mann, 1977; Carpenter, 1988), including on hard defences (Ruitton et al., 2000). One of the most vulnerable life stages of marine invertebrates to changing ocean conditions is the transition from pelagic larvae to benthic juveniles (settlement). Fewer larvae may settle on substrata conditioned in low pH (Albright and Langdon, 2011; Doropoulos et al., 2012; Uthicke et al., 2013) and low pH can reduce growth in the first weeks after settlement (Wolfe et al., 2013a, 2013b). Temperatures outside thermal optima also reduce settlement rates and decrease early post-settlement growth and survival (e.g. Mos et al., 2011; Wangenstein et al., 2013). The effects of the interaction between warming and acidification on sea urchins are complex, difficult to predict, and vary depending on the trait examined (Dworjanyn and Byrne, 2018). While the effects of ocean change on settlement success and artificial substrata on recruitment have been examined individually, there have been no studies that have investigated the interactive influences of these factors on settlement success of any marine animal, and only one study examining such impacts on marine plants (Davis et al., 2017).

We propose that concrete's capacity to increase pH could buffer against ocean acidification, helping calcifiers to resist the negative impacts of ocean acidification. This mechanism may function similar to the way in which carbonate-rich sediments protect bivalves from the adverse effects of low aragonite saturation states and/or low pH (Green et al., 2009). As a first step in testing this proposal, we investigated the potential for substrata in upgraded or new coastal defences to influence the success of marine invertebrates in future oceans by examining the relationships among ocean acidification, ocean warming, and substrata on the settlement success of an ecologically and commercially important sea urchin, *Tripneustes gratilla*. This sea urchin is found throughout the Indo-Pacific, including habitats where there is a high occurrence of hard defences protecting urban centres (e.g. Sydney Harbour, Australia; Okinawa, Japan; Kaneohe Bay, Hawaii) (Lawrence and Agatsuma, 2013). *T. gratilla* are exposed to over-fishing and environmental degradation that have resulted in severe population declines (e.g. Shimabukuro, 1991; Juinio-Menez et al., 1998; Westbrook et al., 2015). *T. gratilla* experiences reduced growth and/or survival across multiple life stages when grown in the warm, acidified conditions predicted for the near future (e.g. Rahman et al., 2009; Byrne et al., 2014; Mos et al., 2016). We hypothesised that compared to natural rock (i.e. granite and greywacke), concrete would increase settlement success and early post-settlement growth and survival of *T. gratilla* held in ocean conditions predicted for the near future.

2. Methods

2.1. Materials

Three common materials used in the construction of hard defences were selected as substrata to test hypotheses: concrete, granite, and greywacke (Bulleri and Chapman, 2010). Materials were obtained in November 2015 from a newly upgraded defensive breakwater at Coffs Harbour, NSW, Australia (30° 18.7'S, 153° 9.1'E), which is constructed from concrete (S40 grade, 40 MPA, BORAL DUR40-20-GP), granite (Valla Monzogranite, see composition for Clarence River Plutonic Suite, Shaw and Flood, 1981), and greywacke (composition described by Korsch, 1981). Along the nearby coast, rocky shores and rocky reefs are primarily composed of greywacke (Korsch, 1978, 1981), while concrete and granite are found only in artificial structures.

2.2. Larval rearing

Larvae used were the offspring of three female and three male *T. gratilla* maintained as broodstock at the National Marine Science Centre, Coffs Harbour (30°12.5'S, 153°16.1'E) at 26–27 °C and pH 8.12 (range 8.0–8.15). Larval culture methods were as described by Mos et al. (2011). Larvae were cultured for 53 days until >75% of larvae possessed multiple pedicellaria and/or tube feet visibly extending from the vestibule, indicative of competency to settle and high post-settlement survival (Mos and Dworjanyn, 2016), at which point they were used in settlement assays.

2.3. Effect of temperature, pH, and substratum on settlement success

To test the hypotheses that concrete would increase settlement success and early post-settlement growth and survival of *T. gratilla* when held in ocean conditions predicted for the near future, an experiment was set up manipulating temperature, pH, and substratum. Competent larvae were added to 18 treatments determined by factorial crosses of two temperatures (24 and 27 °C), three pH conditions (8.1, 7.9, 7.7), and three substrata (concrete, granite, and greywacke). Temperature-pH treatments were representative of mean pH and sea surface temperatures (SST) currently experienced by *T. gratilla* in the southern extent of their range in Australia, and decreases in pH (−0.25 and −0.45 pH units) and warming of 3 °C predicted before the end of the century (Lenton et al., 2015). The high temperature already occurs during warming anomalies (Wernberg et al., 2013; Hughes et al., 2017).

The experiment was conducted in a purpose-built flow-through seawater system with filtered (1 µm) and UV-sterilised seawater delivered independently into rearing containers using dripper taps (0.6–0.8 L.h^{−1}) (see Graba-Landry et al., 2018 for detailed description of seawater system). There were seven replicate rearing containers for each treatment, consisting of 70 mL sample jars with a mesh covered window (45 µm) that acted as an overflow maintaining a 40 mL volume of seawater in the containers. Seawater flowed through three 60 L mixing tanks, where in two of which experimental pH (pH 7.9 and pH 7.7) was regulated by injection of pure CO₂ using an automated CO₂ system and a vortex mixer (Red Sea). Mixing tanks were continuously bubbled with air to aid mixing and to maintain dissolved oxygen >95%. The control pH mixing tank received air bubbling only. Water was then fed into three header tanks where it was heated to the experimental temperatures using aquarium heaters (300 W) controlled by a temperature controller (Tunze). Temperatures and pH of the experimental waters were modified according to conditions in the rearing containers.

Temperature, pH_{NIST} and salinity in the rearing containers in all treatments were measured once per day, four or five times each week ($n = 18$ of 28 days), using a Hach® HQ40d multi-controller, Hach® PHC101 temperature-compensated pH probe and Hach® CDC101 conductivity probe, respectively, calibrated with high precision buffers (Oakton 05942-29, 05942-49, 05942-69). For alkalinity measurements, samples (50 mL) of the seawater supplied to the experiment were collected every second day, filtered (0.25 µm) and fixed with 5 µL of saturated HgCl₂. Total alkalinity (A_T) was measured by potentiometric titration using a Metrohm 888 Titrando and corrected against certified reference standards (Dickson et al., 2007). A_T values from the intake water were used to calculate mean carbonate chemistry parameters in replicates as a pilot experiment found pre-conditioned substrata inoculated with biofilm (described below) had limited effects on the A_T of seawater when kept at three temperatures (23, 25, 27 °C) and three pH levels (8.1, 7.9, 7.7) in the replicate containers and flow-through seawater system for 4 wk. (Fig. A.1). Partial pressure of dissolved CO₂ (pCO₂), carbonate mineral saturation states (Ω_{Ar} and Ω_{Ca}), and bicarbonate (HCO₃[−]) and carbonate (CO₃^{2−}) concentrations were calculated

using CO2SYS (Pierrot et al., 2006) using the dissociation constants of Mehrbach et al. (1973) as refitted by Dickson and Millero (1987) from salinity, temperature, pH_{NIST}, and A_T values measured during the experiments (Table A.1, A.2).

Pieces of substrata (~2 × 2 × 1 cm; concrete, granite, or greywacke) were inoculated with biofilm-forming organisms by placing in an outside raceway with flow-through seawater for 1 wk. To encourage growth of the biofilm on the substrata, the substrata were placed in replicate rearing containers in all experimental water treatments for 3 wk. under 'cool white' fluorescent lighting (32–46 µmol.m^{−2}.sec^{−1}, 12:12 h photoperiod). At the beginning of the experiment, substrata were moved to clean rearing containers to encourage the larvae to settle directly onto the substrata. 20 competent *T. gratilla* larvae were pipetted into each replicate container. After 48 h, settlement was assessed. Larvae were counted as settled if they had everted their rudiment, were attached to a surface via tube feet, and had at least partially absorbed their larval structures. Data were reported as a percentage of the total number of larvae added to each container. Settled juveniles were gently removed using a pipette, photographed, and then returned to their container. The test diameter (TD), number and length of spines, and the occurrence of abnormalities of newly-settled *T. gratilla* were assessed from the photographs using image analysis software (ImageJ, NIH). TD was calculated for each juvenile as the average of two perpendicular measures across the test at the longest axis, and the mean TD in each replicate was used for statistical analysis. Spine length was calculated as the average of the five longest spines from each juvenile. Juveniles were considered to be abnormal if they had at least two of the following characteristics: irregular test shape, abnormal colouration, and >50% smaller than other juveniles in the same treatment (Mos and Dworjanyn, 2016). Abnormal juveniles were excluded from analyses of TD and spine length.

2.4. Effect of temperature, pH, and substratum on post-settlement growth and survival

To examine the effects of temperature, pH and type of substratum on post-settlement survival and growth, newly-settled *T. gratilla* were maintained in the replicate containers after settlement for 4 wk. Survival rates, TD, spine number, and spine length were assessed after 2 wk. and 4 wk. as previously described. Survival rates after 4 wk. were calculated as a percentage of competent larvae added to each replicate. There were insufficient replicates for statistical analysis of TD, spine number, and spine length after 4 wk. due to high mortalities in some treatments, so data from week two were analysed.

2.5. Statistical Analysis

Data for the experiment testing the effects of temperature, pH, and substrata on settlement success and post-settlement growth and survival of *T. gratilla* were analysed using permutational analysis of variance (PERMANOVA, Anderson, 2001). Three-way PERMANOVAs were conducted using temperature, pH, and substrata as fixed factors. The potential for differences in the density of newly-settled *T. gratilla* to influence post-settlement growth and survival was examined by including settlement rate as a covariate in analyses. There was little effect of the inclusion of this covariate on the outcomes of the analyses. Analyses were therefore presented without the covariate. Pair-wise comparisons of untransformed data were generated using Euclidean distance and 9999 permutations of the raw data. Post-hoc pair-wise tests were performed when PERMANOVA results indicated that there were significant differences within treatments with three levels. For reporting post-hoc tests, > and < indicate significantly greater than or less than at $P < 0.05$ respectively, while = indicates no significant difference, $P > 0.05$.

3. Results

3.1. Effect of temperature, pH, and substratum on settlement success

Settlement rates were dependent on an interaction between pH and type of substratum (Fig. 1, Table 1, followed by post-hoc pair-wise tests). Settlement rates were not significantly different among the substrata at pH 8.1 and 7.9, however at pH 7.7, settlement rates were 1.4–1.6 times greater on greywacke and granite than on concrete (concrete < greywacke = granite). When the effect of pH was compared separately for each substratum, settlement rates on granite were 1.4–1.7 times greater at pH 7.7 than pH 8.1 and 7.9 ($8.1 = 7.9 < 7.7$) and ~1.4 times greater at pH 7.9 than pH 8.1 and 7.7 on concrete ($8.1 = 7.7 < 7.9$), but there was no effect of pH for greywacke ($8.1 = 7.9 = 7.7$). Settlement rates were 1.3 times greater at 27 °C than 24 °C, with no interaction with pH or substratum type (Table 1, followed by post-hoc pair-wise tests). There were no other significant interactions (Table 1).

Temperature, pH, and substratum affected the morphology of newly-settled *T. gratilla* (Fig. 2). TD was dependent on an interaction between temperature and pH (Fig. 2a, Table 1, followed by post-hoc pair-wise tests). At 24 °C, TD was ~5% greater at pH 7.9 than pH 8.1 ($8.1 < 7.9$, $8.1 = 7.7$, $7.9 = 7.7$). However at 27 °C, TD was ~5% greater at pH 7.7 than pH 8.1 and 7.9 ($8.1 = 7.9 < 7.7$). When the effect of temperature was compared separately for each pH, TD was always greater at 27 °C than 24 °C, regardless of pH. There were no other significant interactions and no main effect for substratum on TD (Table 1).

The mean number of spines possessed by newly-settled *T. gratilla* was influenced by temperature and pH, but not substratum, and there were no interactions among these factors (Fig. 2b, Table 1, followed by post-hoc pair-wise tests). Juveniles had ~1 fewer spines at 27 °C than at 24 °C ($24 > 27$ °C) and ~1 fewer spines at pH 7.7 than at pH 8.1 and 7.9 ($8.1 = 7.9 > 7.7$).

The mean length of the spines of newly-settled *T. gratilla* was dependent on an interaction between pH and temperature (Fig. 2c, Table 1, followed by post-hoc pair-wise tests). At 24 °C, spines length increased by as much as 19% as pH decreased ($8.1 < 7.9 < 7.7$). However at 27 °C, spine length was not different among pH treatments ($8.1 = 7.9 = 7.7$). When the effect of temperature was compared separately for each pH, at pH 8.1, spines were 12% longer at 27 °C than 24 °C. At pH 7.9, spines were 4% longer at 24 °C than 27 °C. At pH 7.7, however, there was no difference in spine length among temperatures ($24 = 27$ °C). Spine length was also dependent on an interaction between temperature and substrata (Fig. 2c, Table 1, followed by post-hoc pair-wise tests). At 24 °C, there were no differences in spine length among substrata (concrete = greywacke = granite), however at 27 °C, spines were 9% or 15% longer in the concrete treatment than in the granite and greywacke treatments respectively (concrete > greywacke = granite). When the effect of temperature was compared separately for each substratum, spines were 10% longer at 27 °C than 24 °C in the concrete treatment ($24 < 27$ °C).

Table 1

PERMANOVA analyses examining the effects of pH, temperature and substratum type on settlement, test diameter, number of spines, spine length, and occurrence of abnormalities of *Tripteneustes gratilla* after 48 h.

Parameters	Source	df	MS	F	P
Settlement	Temp	1	4.99E3	15.75	<0.001
	pH	2	1.11E3	3.50	0.033
	Sub	2	208.41	0.66	0.517
	Temp × pH	2	243.04	0.77	0.465
	Temp × Sub	2	249.27	0.79	0.452
	pH × Sub	4	995.92	3.14	0.018
	Temp × pH × Sub	4	57.72	0.18	0.948
Test diameter	Residual	107	316.87		
	Temp	1	7.55E-2	66.92	<0.001
	pH	2	4.54E-3	4.02	0.022
	Sub	2	1.58E-3	1.40	0.244
	Temp × pH	2	3.80E-3	3.37	0.038
	Temp × Sub	2	1.22E-3	1.08	0.339
	pH × Sub	4	4.42E-5	0.04	0.998
Spine count	Temp × pH × Sub	4	8.83E-4	0.78	0.537
	Residual	98	1.13E-3		
	Temp	1	40.59	13.90	<0.001
	pH	2	14.76	5.06	<0.009
	Sub	2	2.06	0.71	0.492
	Temp × pH	2	1.36	0.46	0.621
	Temp × Sub	2	0.48	0.16	0.850
Spine length	pH × Sub	4	2.27	0.78	0.536
	Temp × pH × Sub	4	2.07	0.71	0.586
	Residual	100	2.92		
	Temp	1	2.83E-3	2.86	0.089
	pH	2	8.93E-3	9.03	<0.001
	Sub	2	6.02E-3	6.08	<0.003
	Temp × pH	2	5.27E-3	5.33	<0.006
Abnormalities	Temp × Sub	2	4.15E-3	4.19	0.018
	pH × Sub	4	1.97E-3	1.98	0.104
	Temp × pH × Sub	4	5.90E-4	0.59	0.677
	Residual	99	9.90E-4		
	Temp	1	7.30E3	23.38	<0.001
	pH	2	212.44	0.68	0.510
	Sub	2	2.21E3	7.09	<0.001
	Temp × pH	2	311.95	1.00	0.362
	Temp × Sub	2	1.19E3	3.82	0.023
	pH × Sub	4	370.46	1.19	0.318
	Temp × pH × Sub	4	342.58	1.10	0.363
	Residual	97	312.27		

Temp, temperature; Sub, substratum; significant differences ($P < 0.05$) are in bold; df, degrees of freedom; MS, mean square.

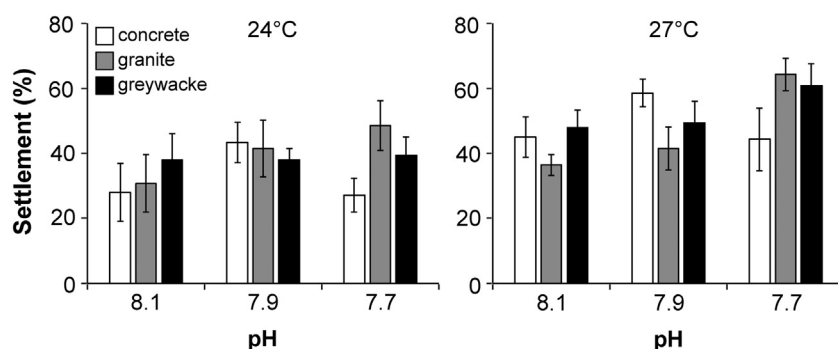


Fig. 1. The effect of temperature, pH, and substratum on the settlement of *Tripteneustes gratilla*. Settlement was dependent on an interaction between pH and substratum, and a main effect of temperature only (Table 1, followed by post-hoc pair-wise tests, in text). Data are means \pm S.E., $n = 7$, except for the 24 °C/pH 7.9/concrete treatment where $n = 6$.

Nonetheless, there were no differences in spine length among temperatures in the granite and greywacke treatments ($24 = 27$ °C). There were no other significant interactions among factors (Table 1).

The occurrence of abnormalities among newly-settled *T. gratilla* was dependent on an interaction between temperature and substrata, with no other significant interactions and no main effect of pH (Fig. 2d, Table 1, followed by post-hoc pair-wise tests). At 24 °C, the rate at which abnormalities occurred was approximately halved in the

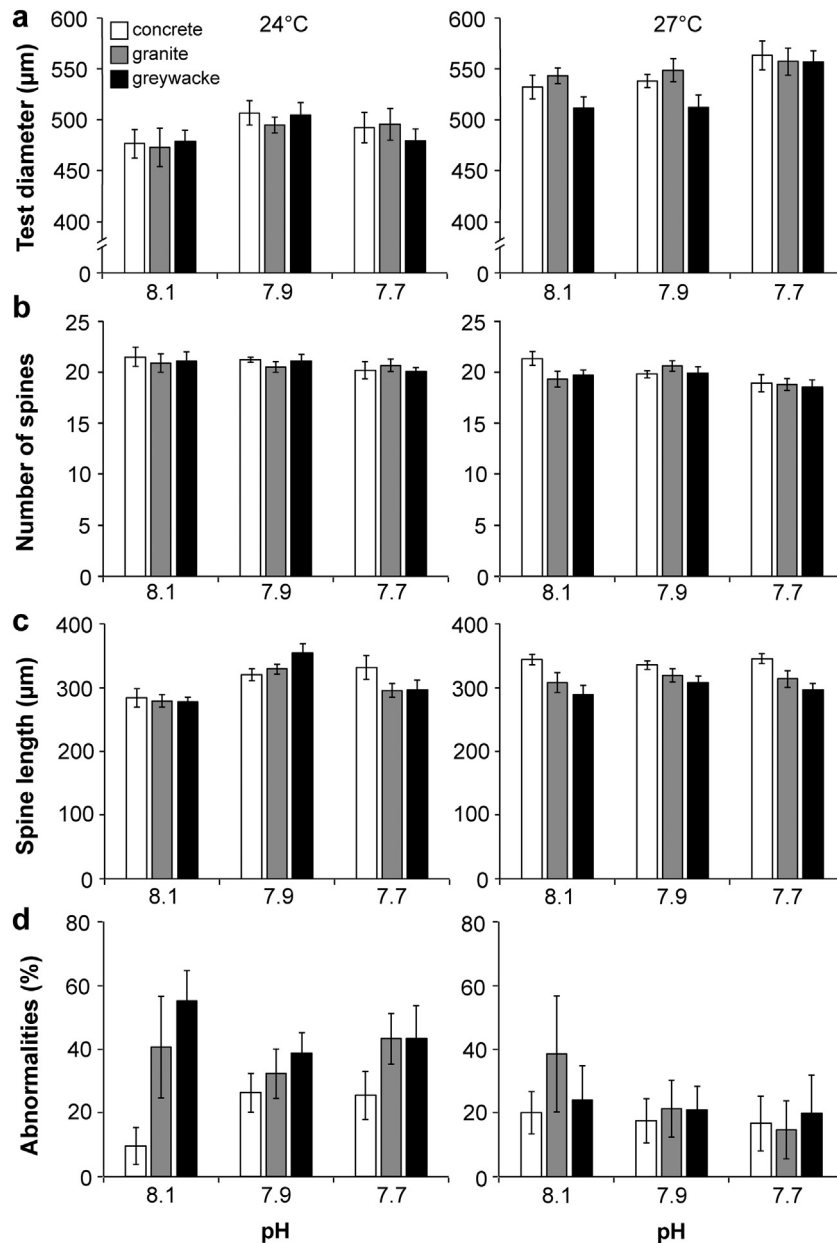


Fig. 2. The effect of temperature, pH, and substratum on the morphology of newly-settled *Tripneustes gratilla* after 48 h: (a) test diameter (TD), (b) number of spines, (c) spine length, (d) occurrence of abnormalities. TD was dependent on an interaction between temperature and pH (Table 1, followed by post-hoc pair-wise tests, in text). Spine counts were dependent on temperature and pH (Table 1, followed by post-hoc pair-wise tests, in text). Spine length was dependent on an interaction between pH and temperature (Table 1, followed by post-hoc pair-wise tests, in text). The occurrence of abnormalities was dependent on an interaction between temperature and substratum (Table 1, followed by post-hoc pair-wise tests, in text). Data are means \pm S.E., $n = 4-7$.

concrete treatment compared to the greywacke and granite treatments (concrete < greywacke = granite). However at 27 °C, there was no difference in the occurrence rates of abnormalities among substrata (concrete = greywacke = granite). When the effects of temperature were compared for each substratum, abnormalities occurred 1.8–2.4 times more at 24 °C than 27 °C in the greywacke and granite treatments, but there was no difference in the occurrence of abnormalities in the concrete treatment at different temperatures (24 = 27 °C).

3.2. Effect of temperature, pH, and substratum on post-settlement morphology and growth

pH and substrata affected the morphology of newly-settled *T. gratilla* after 2 wk., but temperature had little effect (Fig. 3). Test diameter (TD) was dependent on an interaction between pH and substratum (Fig. 3a,

Table 2, followed by post-hoc pair-wise tests). At pH 8.1, TD was 15% greater in the greywacke treatment than in the granite treatment (greywacke > granite, concrete = greywacke, concrete = granite). At pH 7.9, TD was 12% greater in the concrete treatment than in the greywacke and granite treatments (concrete > greywacke = granite). At pH 7.7, TD was 18% and 13% greater in the concrete and granite treatments, respectively, than in the greywacke treatment (concrete = granite > greywacke). When the effect of pH was compared separately for each substratum, TD in the greywacke treatment was reduced by as much as 20% as pH decreased (8.1 > 7.9 > 7.7). However, there was no effect of pH for granite or concrete (8.1 = 7.9 = 7.7). There were no other significant interactions and no main effect for temperature (Table 2).

The mean number and length of spines possessed by *T. gratilla* after 2 wk. post-settlement was dependent on pH, but not substrata or

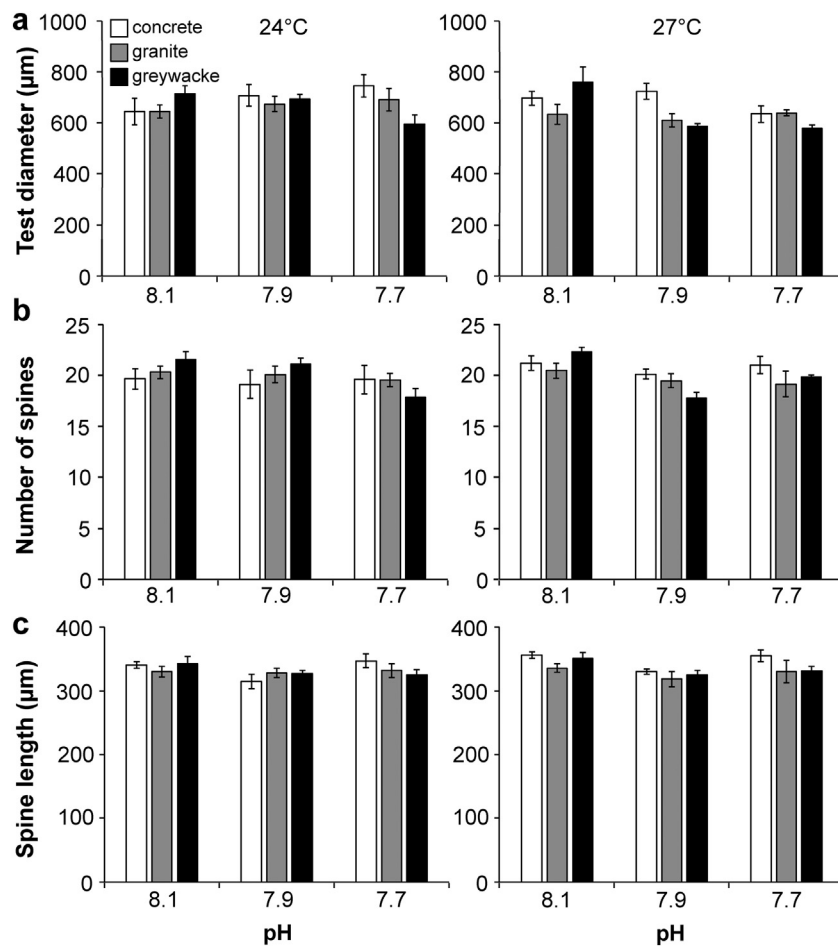


Fig. 3. The effect of temperature, pH, and substratum on the morphology of newly-settled *Tripneustes gratilla* after 2 wk: (a) test diameter (TD), (b) number of spines, (c) spine length. TD was dependent on a significant interaction between pH and substratum (Table 2, followed by post-hoc pair-wise tests, in text). The number of spines and spine length were dependent on pH only (Table 2, followed by post-hoc pair-wise tests, in text). Data are means \pm S.E., $n = 3-7$.

temperature, and there were no interactions among these factors (Fig. 3b–c, Table 2, followed by post-hoc pair-wise tests). Juveniles possessed ~1.3 more spines at pH 8.1 than at pH 7.9 and 7.7 ($8.1 > 7.9 = 7.7$). Spines were 4–6% longer at pH 8.1 and 7.7 than at pH 7.9 ($8.1 = 7.7 > 7.9$).

3.3. Effect of temperature, pH, and substratum on post-settlement survival

Survival of competent *T. gratilla* larvae to 4 wk. post-settlement was dependent on an interaction between temperature and substrata (Fig. 4, Table 2, followed by post-hoc pair-wise tests). At 24 °C, survival rates were not different among substrata (concrete = greywacke = granite), but at 27 °C, survival rates were ~2 times greater in the concrete treatments than in the granite treatments (concrete = greywacke, concrete > granite, greywacke = granite). When the effect of temperature was compared separately for each substratum, survival rates in the granite treatment were 3.3 times greater at 24 °C than at 27 °C, but there was no effect of temperature for greywacke or concrete ($24 = 27$ °C). Survival was also dependent on pH only (Table 2, followed by post-hoc pair-wise tests). Survival rates were 1.5–1.7 times greater at pH 8.1 and 7.9 than at pH 7.7 ($8.1 = 7.9 > 7.7$). There were no other significant interactions among factors (Table 2).

4. Discussion

We found mixed support for our hypotheses that concrete could improve settlement rates and post-settlement growth and survival of the sea urchin *Tripneustes gratilla* in near-future ocean warming and

acidification conditions. Our results indicate that there is potential for low-carbon concrete to assist marine organisms in coping with global climate stressors, but highlight the need for further research to demonstrate how marine organisms interact with concrete and other engineered materials.

Concrete had some positive effects for *T. gratilla* exposed to temperature and pH conditions predicted for future oceans. In low pH conditions (pH 7.9, 7.7), juveniles on concrete were larger than juveniles on greywacke after 2 wk. In warmed conditions (27 °C), *T. gratilla* that settled on concrete had longer spines than settlers on greywacke or granite, and there were more juveniles on concrete than on granite after 4 wk. In addition, there were fewer abnormal *T. gratilla* on concrete than on greywacke or granite at 24 °C after 48 h. The positive effects of concrete on *T. gratilla* may be driven by concrete's influence on water chemistry. The release of alkali chemicals from concrete increases pH and the availability of carbonate in surrounding water (Anderson and Underwood, 1994; Davies et al., 2010; Wright et al., 2011), and these effects are likely to be greatest near the material's surface (i.e. within the diffusion boundary layer (DBL), sensu Hurd et al., 2011). High calcite saturation states and/or pH in DBLs may protect newly-settled organisms from low pH conditions in surrounding water (Green et al., 2009; Green et al., 2013), and possibly boost post-settlement growth and survival by reducing the energetic costs of acid-base regulation and increasing the amount of energy directed to formation of calcified body parts (Catarino et al., 2012; Stumpp et al., 2012). In addition, concrete may alter the availability of non-alkali chemicals, with the potential to influence the fitness of newly settled invertebrates through changes in the quantity and quality of their food (biofilms). For example cement,

Table 2

PERMANOVA analyses examining the effects of pH, temperature and substratum type on test diameter, number of spines, and spine length of *Tripneustes gratilla* after 2 wk., and post-settlement survival after 4 wk.

Parameters	Source	df	MS	F	P
Test diameter	Temp	1	1.79E4	2.50	0.119
	pH	2	1.04E4	1.46	0.245
	Sub	2	1.92E4	2.68	0.073
	Temp × pH	2	2.06E4	2.88	0.061
	Temp × Sub	2	1.62E3	0.23	0.798
	pH × Sub	4	3.27E4	4.58	<0.002
	Temp × pH × Sub	4	1.02E4	1.43	0.229
Spine count	Residual	91	7.15E3		
	Temp	1	1.52	0.40	0.523
	pH	2	21.73	5.69	0.004
	Sub	2	0.73	0.19	0.829
	Temp × pH	2	11.06	2.89	0.062
	Temp × Sub	2	7.11	1.86	0.168
	pH × Sub	4	7.60	1.99	0.100
Spine length	Temp × pH × Sub	4	7.17	1.88	0.128
	Residual	91	3.82		
	Temp	1	680.63	1.41	0.240
	pH	2	3.37E3	6.99	<0.002
	Sub	2	1.11E3	2.31	0.102
	Temp × pH	2	176.99	0.37	0.697
	Temp × Sub	2	477.14	0.99	0.374
Survival	pH × Sub	4	815.76	1.69	0.156
	Temp × pH × Sub	4	83.49	0.17	0.950
	Residual	91	482.31		
	Temp	1	1.00E3	4.65	0.035
	pH	2	1.01E3	4.70	0.011
	Sub	2	147.56	0.69	0.501
	Temp × pH	2	59.61	0.28	0.760
	Temp × Sub	2	675.80	3.14	0.046
	pH × Sub	4	118.62	0.55	0.700
	Temp × pH × Sub	4	63.50	0.30	0.881
	Residual	107	214.93		

Temp, temperature; Sub, substratum; significant differences ($P < 0.05$) are in bold; df, degrees of freedom; MS, mean square.

a primary ingredient in concrete, can reduce the availability of nitrate, phosphate, and sulfate (Park et al., 2008). Nitrogen limitation inhibits growth and alters the nutritional quality of algae by reducing protein synthesis and enhancing the accumulation of lipids (e.g. Richardson et al., 1969; Falkowski et al., 1989). In order to fully test our hypothesis that the benefits of concrete were derived from the influence of concrete on water chemistry, carbonate chemistry and the availability of nutrients in the DBL would need to be measured in situ, which was not done in this study. Future studies examining the interactive effects of concrete and climate stressors on marine organisms will therefore need to consider the effects of concrete and biofilms on DBL water chemistry, and the role of DBL water chemistry and biofilms in directly or indirectly determining the fitness of newly settled marine organisms.

Concrete was not always a superior substratum to natural rock for *T. gratilla*. At pH 7.7, fewer larvae settled on concrete than on greywacke or granite. The different substrata also had little effect on TD after 48 h, spine counts after 48 h and 2 wk., or spine lengths after 2 wk. We found little evidence to suggest that differences in post-settlement growth and survival among substrata were driven by variation in settlement rates and subsequent density of newly settled *T. gratilla*. It may be that the disparate effects of the substrata on the fitness and morphology of *T. gratilla* were associated with the community composition and structure of the biofilm that colonised their surfaces rather than food availability per se. While we did not quantify biofilm composition, studies that have compared the effects of different substrata on biofilms have highlighted the capacity of substrata to determine the development, community composition, and structure of biofilms (e.g. Marszałek et al., 1979; Faimali et al., 2004; Sempere-Valverde et al., 2018). For example, substrata that actively leach materials are often colonised by microbes more slowly than comparatively inert materials (Marszałek et al., 1979). Microbial biofilms play a crucial role in inducing settlement of marine larvae (Hadfield, 2011) and as food for post-larvae, including *T. gratilla* (Dworjanyn and Pirozzi, 2008; Mos et al., 2011). Differences in the abundance of chemical settlement cues and food associated with variation in biofilm colonisation and community composition among substrata may therefore explain why fewer *T. gratilla* larvae settled on concrete than greywacke or granite, and why survival rates after 4 wk. were ~2 times greater on concrete than the other substrata. The combined effects of substrata and their associated biofilms on invertebrates are also likely to be influenced by ocean conditions predicted for the near future (Baragi and Anil, 2016). High temperatures and low pH promote the colonisation of concrete by turfing algae (Davis et al., 2017), which can inhibit successive colonisation by fleshy macroalgae and invertebrates (e.g. Kennelly, 1987; Birrell et al., 2005). Future studies examining the effects of pH-buffering materials on recruitment and fitness of benthic marine animals may therefore need to partition the effects of ocean change stressors, substrata, and the ecological communities which colonise the substrata.

The transition from pelagic larvae to benthic juveniles is one of the most vulnerable life stages of marine invertebrates to global stressors (Byrne and Przesławski, 2013; Kroeker et al., 2013). We found low pH conditions (pH 7.9, 7.7) generally reduced the size and number of *T. gratilla* that completed this transition. Other studies that have examined the effects of ocean acidification on sea urchins have also found negative effects of low pH on early post-settlement growth, morphology, and survival (Dupont et al., 2013; Wolfe et al., 2013a, 2013b). The negative effects of ocean acidification on newly-settled marine invertebrates are thought to be driven by suppression of metabolic and/or calcification rates by low pH and/or high CO₂ (Nakamura et al., 2011; Moya et al., 2012; Lane et al., 2013; Wolfe et al., 2013a). In contrast, we found increased temperature had negligible or positive effects on newly-

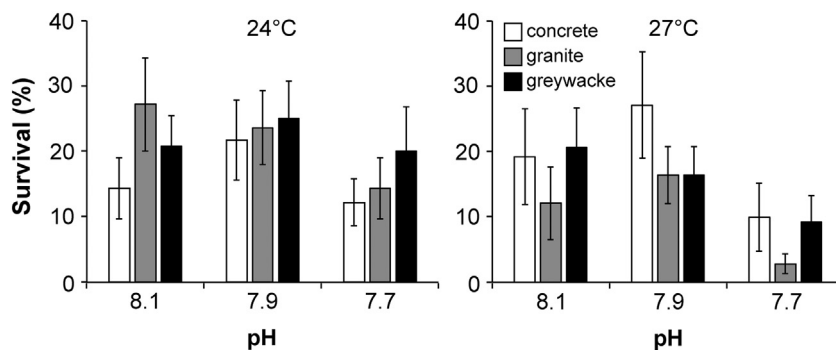


Fig. 4. The effect of temperature, pH, and substratum on the survival of competent *Tripneustes gratilla* larvae to 4 wk. post-settlement. Survival was dependent on a significant interaction between temperature and substratum, and a main effect of pH only (Table 2, followed by post-hoc pair-wise tests, in text). Data are means \pm S.E., $n = 7$, except for the 24 °C/pH 7.9/ concrete treatment where $n = 6$.

settled *T. gratilla*, possibly because the highest temperature used in this study (27 °C) is close to the thermal optima of this species during settlement (Mos et al., 2011). This result underscores the importance of moderate warming in countering the negative effects of low pH on *T. gratilla* living at the higher latitude edge of its distribution (also see Sheppard-Brennand et al., 2010; Dworjanyn and Byrne, 2018), and highlights the need for future studies to test multiple stressors when examining the effects of engineered materials on marine organisms in future ocean conditions.

The negative effects of ocean change in reducing post-settlement growth and survival of sea urchins are concerning given that patterns in larval recruitment can dictate the distribution and abundance of adults (Underwood and Keough, 2001). Declines in the abundance of sea urchins can cause ecological regime shifts through release of grazing control of seaweeds (e.g. Hughes, 1994; Steneck et al., 2013). Our results indicate that there is potential for concrete to boost the recruitment of sea urchins on hard defences, helping to restore sea urchin populations near major urbanised centres that have experienced severe declines in recent decades due to overfishing and pollution.

There is growing awareness that coastal protection infrastructure can provide social, economic or amenity benefits to society, while minimising adverse environmental impacts (Dafforn et al., 2015). The results of this study and Davis et al. (2017) demonstrate that pH-buffering materials have potential to realise the multifunctional potential of artificial structures in marine systems. Incorporating pH-buffering materials such as concrete into hard defences could promote the recruitment of ecologically and economically important marine calcifiers. Additionally, pH-buffering concrete could be readily combined with existing technologies that increase habitat complexity to further boost recruitment (reviewed by Strain et al., 2018). An important caveat is that our results were obtained during a short-term study conducted under stable conditions in the laboratory. More research is required to understand the way in which the effectiveness of pH-buffering materials may be affected by the complex interactions among substrata, colonising organisms, and environmental stressors, and to test the effectiveness and longevity of pH-buffering materials in the field. The potential environmental benefits of pH-buffering materials will also need to be weighed against the environmental impacts of producing these materials.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2018.07.379>.

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